

Random networks of carbon nanotubes as an electronic material

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We report on the transport properties of random networks of single-wall carbon nanotubes fabricated into thin-film transistors. At low nanotube densities ($\sim 1 \mu\text{m}^{-2}$) the networks are electrically continuous and behave like a p -type semiconductor with a field-effect mobility of $\sim 10 \text{ cm}^2/\text{Vs}$ and a transistor on-to-off ratio $\sim 10^5$. At higher densities ($\sim 10 \mu\text{m}^{-2}$) the field-effect mobility can exceed $100 \text{ cm}^2/\text{Vs}$; however, in this case the network behaves like a narrow band gap semiconductor with a high off-state current. The fact that useful device properties are achieved without precision assembly of the nanotubes suggests the random carbon nanotube networks may be a viable material for thin-film transistor applications. [DOI: 10.1063/1.1564291]

Perhaps the most intriguing electronic property of single-wall carbon nanotubes (SWNTs) is the high room-temperature mobility of semiconducting SWNTs (s-SWNTs) that is more than an order of magnitude larger than the mobility of crystalline Si.^{1,2} This high mobility has prompted researchers to fabricate and study field-effect transistors in which a single s-SWNT serves as a high-mobility transport channel.¹⁻⁷ Recent measurements on such devices yield a transconductance per unit channel width greater than that of state-of-the-art Si transistors.⁷ However, because of the limited current-carrying capacity of individual SWNTs, many s-SWNTs aligned side by side in a single device would be required in order to surpass the current drive of a Si device. Such precise positioning of SWNTs is beyond the capability of current growth and assembly technology and presents a major technological hurdle for carbon nanotube-based electronic applications.

In contrast, random arrays of SWNTs are easily produced either by direct growth on a catalyzed substrate or by deposition onto an arbitrary substrate from a solution of suspended SWNTs. If the density of SWNTs in such an array is sufficiently high, the nanotubes will interconnect and form continuous electrical paths. Such random arrays of SWNTs have not previously been seriously investigated for use as channels in field-effect transistors.

In this letter we explore the transport properties of random networks of SWNTs and find that low density networks ($\sim 1 \mu\text{m}^{-2}$) behave like a p -type semiconducting thin film with a field-effect mobility $\sim 10 \text{ cm}^2/\text{Vs}$, approximately an order of magnitude larger than the mobility of materials typically used in commercial thin-film transistors, e.g., amorphous Si. These mobility values and correspondingly good electronic quality of the random SWNT network are due to a combination of the low resistance of inter-SWNT contacts and the high mobility of the individual SWNTs, which together compensate for the extremely low fill factor of the network. These initial transport results are promising and indicate that such random nanotube networks (easily produced with no need for precision assembly) form an interest-

ing electronic material that has potential for use in thin-film transistor applications to produce active electronics on noncrystalline or compliant substrates.

The transport properties of the SWNT networks were measured in a thin-film transistor geometry. SWNTs were grown on a 250-nm-thick thermal oxide on a Si wafer.⁸ Source-drain electrodes were fabricated using optical lithography and lift-off of a 150-nm-thick Ti film. The regions of the devices between the source-drain electrodes were then covered with photoresist and the nanotubes outside this protected area were removed by using a CO_2 snow jet. Finally, the protective photoresist was removed and the devices were tested in a vacuum probe station.

A schematic of the device is shown in Fig. 1. The device geometry was varied with the source-drain channel length, L_{sd} , ranging from 1 to $25 \mu\text{m}$ and the channel width, W , ranging from 35 to $100 \mu\text{m}$. Figure 1 also shows an atomic force microscope (AFM) image of a SWNT network in the region between the source-drain electrodes. Such images and AFM line profiles were used to determine the diameter (d), density (ρ), and length (L) of the nanotubes where ρ is defined as the number of SWNTs per unit area.

For most of the devices the average nanotube length, $\langle L \rangle$,

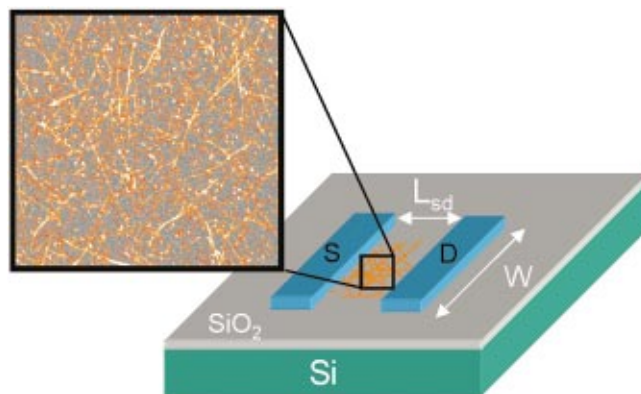


FIG. 1. (Color) (A) Schematic of the device geometry. The SWNT network is grown on top of the thermal oxide of a conducting Si substrate. Evaporated titanium forms the source and drain contact pads and the Si substrate serves as a back gate. (B) A $5 \mu\text{m} \times 5 \mu\text{m}$ AFM image of a SWNT network. Such images and AFM line traces were used to measure the average nanotube diameter, length, and density.

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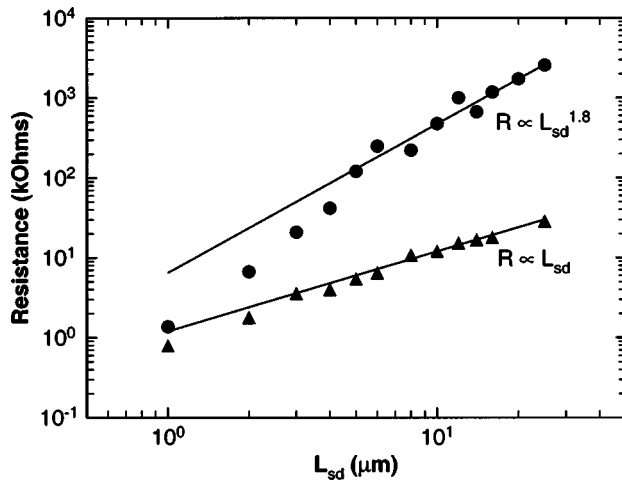


FIG. 2. Electrical resistance measurements on devices with a channel width of 90 μm and channel lengths ranging from 1 to 25 μm . The resistance measurements were made at a gate bias of -3 V. The two sets of data correspond to two separate growths that produced nanotube densities of 1 (●) and 10 (μm^{-2}).

is much shorter than L_{sd} , which means that the source-drain current has to flow through a series of inter-nanotube contacts. Fuhrer *et al.*⁹ have shown that the intersection of two s-SWNTs or two metallic SWNTs forms a good electrical contact with an electrical conductance $\sim 0.1 e^2/h$ and that the intersection of a metallic and a s-SWNT forms a Schottky barrier with a barrier height approximately equal to $1/2$ band gap of the s-SWNT. Consequently, we expect that highly interconnected SWNT arrays will be electrically continuous with electronic properties that depend on the level of interconnectivity and on the electronic properties of the constituent SWNTs.

This system of electrically connected randomly positioned SWNTs is in many ways analogous to the two-dimensional random resistor networks studied in percolation theory.^{10,11} Such resistor networks are electrically conducting provided that the density of connected resistors exceeds a percolation threshold. In addition, the sample-to-sample variations are vanishingly small provided that the size of the resistor lattice is large compared to the lattice spacing. In the present case we estimate that the percolation threshold will correspond approximately to the density at which the average distance between nanotubes, $1/\rho^{1/2}$, equals their average length, i.e., $\rho_{th} \sim 1/\langle L \rangle^2$ and that the network properties will be relatively uniform provided that the device dimensions are much larger than $1/\rho^{1/2}$. Above the percolation threshold there is a high likelihood that the SWNTs will intersect with one another and form continuous electrical paths. For our growth conditions we have measured samples with $\langle L \rangle$ ranging from 1 to 3 μm and find that for SWNT densities exceeding $\sim 0.3 \mu\text{m}^{-2}$ the networks are electrically conducting.

The geometric scaling of the device resistance is shown in Fig. 2 which plots the log of the source to drain resistance¹² versus $\log(L_{sd})$ for two sets of devices corresponding to $\rho = 10$ and $1 \mu\text{m}^{-2}$. The resistance data for the $10 \mu\text{m}^{-2}$ network scale linearly with channel length with a sheet resistance of 108 k Ω /square. The resistance data for the $1 \mu\text{m}^{-2}$ network scale nonlinearly with channel length, and a least squares power law fit to the data for $L_{sd} \geq 5 \mu\text{m}$ yields

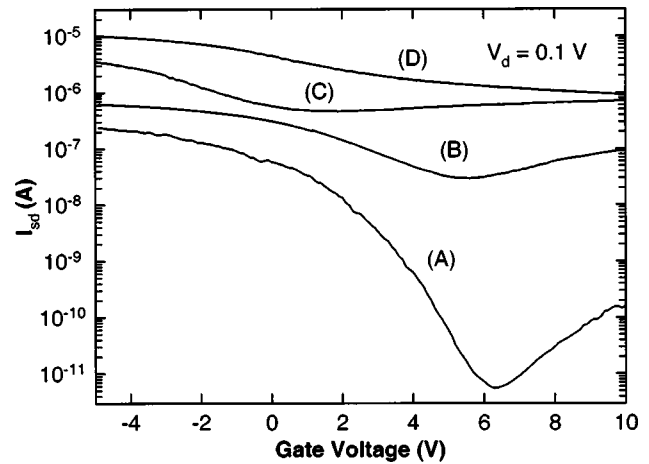


FIG. 3. $\log(I_{sd})$ vs V_g at $V_d = 0.1$ V for four devices from four different growths, corresponding to curves (a)–(d), each with a channel width of 35 μm and a channel length of 10 μm . The gate dependence indicates that the networks behave like a p -type semiconducting film with field-effect mobilities ranging from 7 to 270 cm^2/Vs . Only the network corresponding to curve (a) can be gated off.

$R \propto L^{1.8}$. This nonlinear scaling is an indication that the network is approaching the percolation threshold where nonlinear effects are expected. Note that the short channel length devices with $L_{sd} \sim \langle L \rangle$ scale more rapidly with L_{sd} . In these devices individual SWNTs can directly bridge the source-drain electrodes and thus lower the resistance.

The above resistance data establish that the intersecting SWNTs form an electrically continuous interconnected network. We have measured the gate response of I_{sd} to determine whether the networks exhibit a semiconducting or metallic behavior. Figure 3 [curve (a)] plots the transistor characteristics for the $\rho = 1 \mu\text{m}^{-2}$ network with device dimensions of $L_{sd} = 10 \mu\text{m}$ and $W = 35 \mu\text{m}$. This device exhibits an on-to-off ratio of $\sim 10^5$ and a threshold voltage of 2 V. The observed field effect is likely a combination of two effects: the field dependence of the carrier concentration in the s-SWNTs and the gating of the Schottky barriers present at the nanotube/Ti contacts^{5,6,13} and at the semiconductor/metallic inter-nanotube contacts.^{9,13} The magnitude and polarity of the gate dependence indicate that the network behaves like a p -type semiconducting thin film. We use the standard formula, $\mu_{eff} = dI_{sd}/dV_g L_{ox} L_{sd} / \epsilon V_{sd} W$, to define an effective mobility for the network where L_{ox} and ϵ are the thickness and dielectric constant of the SiO_2 gate oxide. For this network we find $\mu_{eff} = 7 \text{ cm}^2/\text{Vs}$, which is a typical value for devices with high on-off ratio, although we occasionally measure values as high as 50 cm^2/Vs . For comparison, these values are about an order of magnitude larger than the mobility of amorphous Si ($\mu_{eff} \approx 1 \text{ cm}^2/\text{Vs}$), a material commonly used in commercial thin film transistor applications.¹⁴ Note that I_{sd} reaches a minimum at $V_g \approx 6$ V and then increases for larger gate bias. This reversal in slope indicates that the gate potential has inverted some of the electrical paths to n -type conduction. Such inversion from p -type to n -type conduction has been previously noted in field-effect measurements on individual s-SWNTs^{5,15} and establishes a lower limit to the off-state current.

Also plotted in Fig. 3 are data from three other devices [curves (b), (c), and (d)] fabricated using networks with ρ

$>3 \mu\text{m}^{-2}$. The linear gate dependence of the on-state current yields field-effect mobilities ranging from 17 to 270 cm^2/Vs . However, in each of the devices the on-to-off ratio is ≤ 10 . In these devices, the increase in on-state current is achieved at the expense of a high off-state current which in curves (b) and (c) are caused by inversion to n -type conduction. We have observed this high off-state current in all of the tested devices with either high densities, $\rho \gg \rho_{\text{th}}$, or short channel lengths, $L_{\text{sd}} \sim \langle L \rangle$. The inversion to n -type conduction at low gate bias accompanied by a high off-state current is consistent with the behavior of a narrow band gap semiconductor. We thus attribute the high off-state current in these devices to continuous paths of narrow band gap and metallic nanotubes.

The band gap of a s-SWNT scales inversely with its diameter.¹⁶ We therefore postulate that the high off-state current of dense networks is caused by continuous paths of large diameter ($>2 \text{ nm}$) and metallic nanotubes. In such cases the density of metallic and large-diameter SWNTs exceeds the percolation threshold and forms continuous paths across the device. Consequently, the off-state current in random networks will be dominated either by the largest diameter s-SWNTs or by metallic nanotubes, provided their density exceeds ρ_{th} . From AFM line traces we find $\langle d \rangle = 1.7 \text{ nm}$ and that for our growth conditions approximately one third of the nanotubes in the network have a diameter $>2 \text{ nm}$ corresponding to a band gap $<0.35 \text{ eV}$.¹⁷ At high nanotube densities, the density of narrow band gap nanotubes can exceed ρ_{th} and the network will form narrow-band gap conduction paths.

These data suggest that it should be possible to improve the off-state current by reducing the fraction of large-diameter nanotubes. Li *et al.* have shown that the diameter of a single-wall nanotube is approximately equal to the diameter of its catalyst particle.¹⁸ Consequently, one key to higher density nanotube networks with improved on-to-off ratio is careful control of the catalyst particle size.

Because the networks consist of both semiconducting and metallic nanotubes, if the density of metallic nanotubes exceeds the percolation threshold then the network will become metallic. Clearly, in order to achieve the highest current drive with good off-state characteristics, the fraction of both metallic and large diameter nanotubes will have to be reduced. Current growth technology yields approximately 30% metallic SWNTs.¹⁹ The reduction of this fraction is technologically challenging because it requires control over the chirality of the SWNT during growth¹⁶ or some post-growth means of separating metallic from semiconducting nanotubes. Alternatively, Collins, Arnold, and Avouris have shown that applying a large source-drain bias while gating off any semiconducting nanotubes can selectively burn metallic (and possibly low band gap semiconducting) nanotubes.^{15,20} This technique may work as well with nanotube networks to remove those conduction paths that limit the device turn-off characteristics.

The limitations presently experienced with off-state currents arising from parasitic metallic and/or narrow-band gap s-SWNTs should yield to improved control over SWNT growth or selective burnout of the parasitic tubes.¹⁵ While the nanotube networks treated in this letter were formed by direct growth of the nanotubes on the surface, such networks could just as easily be fabricated by depositing previously grown SWNTs onto the substrate. This would allow the fabrication of thin-film transistors without exposing the substrates to high temperatures, thus permitting a wide variety of substrates, including plastic and compliant substrates. Because several techniques have been demonstrated for selectively converting s-SWNTs from p to n type for complementary logic applications,^{21–24} it is likely that random networks can be selectively converted to n type for such applications as well. Random networks of SWNTs may thus offer the most immediate opportunity for carbon nanotubes to impact electronic applications.

- ¹M. Shim, A. Javey, N. W. S. Kam, and H. Dai, *J. Am. Chem. Soc.* **123**, 11512 (2001).
- ²M. S. Fuhrer, B. M. Kim, T. Durkop, and T. Brintlinger, *Nano Lett.* **2**, 755 (2002).
- ³S. Tans, A. Verschuere, and C. Dekker, *Nature (London)* **393**, 49 (1998).
- ⁴R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, *Appl. Phys. Lett.* **73**, 2447 (1998).
- ⁵R. Martel, V. Derycke, C. Lavoie, J. Appenzeller, K. Chen, J. Tersoff, and Ph. Avouris, *Phys. Rev. Lett.* **87**, 256805 (2001).
- ⁶S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, *Phys. Rev. Lett.* **89**, 106801 (2002).
- ⁷S. Wind, J. Appenzeller, R. Martel, V. Derycke, and Ph. Avouris, *Appl. Phys. Lett.* **80**, 3817 (2002).
- ⁸J. H. Hafner, C. L. Cheung, T. H. Ooster Kamp, and C. M. Lieber, *J. Phys. Chem. B* **105**, 743 (2001).
- ⁹M. S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y. G. Yoon, M. S. C. Mazzoni, H. J. Choi, J. Ihm, S. G. Louie, A. Zettl, and P. L. McEuen, *Science* **288**, 494 (2000).
- ¹⁰D. J. Frank and C. J. Lobb, *Phys. Rev. B* **37**, 302 (1988).
- ¹¹M. A. Dobson and J. C. Garland, *Phys. Rev. B* **32**, 7621 (1985).
- ¹²The network resistance was measured with a gate bias of -3 V that was applied to ensure that the semiconducting nanotubes in the network were conducting.
- ¹³T. W. Tombler, C. Zhou, J. Kong, and H. Dai, *Appl. Phys. Lett.* **76**, 2412 (2000).
- ¹⁴B. Stannowski, R. E. I. Schropp, R. B. Wehrspohn, and M. J. Powell, *J. Non-Cryst. Solids* **299–302**, 1340 (2002).
- ¹⁵P. G. Collins, M. S. Arnold, and Ph. Avouris, *Science* **292**, 706 (2001).
- ¹⁶M. Dresselhaus, G. Dresselhaus, and Ph. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties and Applications* (Springer, Berlin, 2001).
- ¹⁷J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, *Nature (London)* **391**, 59 (1998).
- ¹⁸Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang, and H. Dai, *J. Phys. Chem. B* **105**, 11424 (2001).
- ¹⁹W. Kim, H. C. Choi, M. Shim, Y. Li, D. Wang, and H. Dai, *Nano Lett.* **2**, 703 (2002).
- ²⁰Initial attempts to selectively burn the metallic paths and leave a large number of semiconducting paths have not been successful.
- ²¹J. Kong, C. Zhou, E. Yenilmez, and H. Dai, *Appl. Phys. Lett.* **77**, 3977 (2001).
- ²²V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris, *Nano Lett.* **1**, 453 (2001).
- ²³Ph. Avouris, *Chem. Phys.* **281**, 429 (2002).
- ²⁴A. Javey, Q. Wang, A. Ural, Y. Li, and H. Dai, *Nano Lett.* **2**, 929 (2002).